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# THE INTERIONIC ATTRACTION THEORY OF ELECTROLYTES

By Dr. D. A. MacINNES

THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH

IN 1883 Arrhenius advanced the theory that in solutions of salts, acids and bases the molecules are, partly at least, split up into positively and negatively charged *ions*. Thus, for example, an aqueous solution of sodium chloride was conceived to consist in large part of positively charged sodium ions and negatively charged chloride ions, which may be represented by $Na^+$ and $Cl^-$. The theory encountered vigorous opposition, based mostly on the apparently quite reasonable objections that sodium, for instance, which is well known to be a soft inflammable metal, could hardly be present in water, and also, that if positive and negative ions are as close together as they must be in a solution they would certainly be expected to attract each other and recombine. In spite of these objections and others, the theory gained adherents rapidly since it accounted more or less adequately for the main facts about solutions of what we now term electrolytes. The most important facts about such solutions are that, in the first place, they are conductors of electricity and, in addition, that they exhibit abnormal thermodynamic properties, by which we mean that, for example, they produce exceptionally large depressions of the freezing points and vapor pressures of the solvents in which they are dissolved.

The mental picture with which Arrhenius worked was somewhat as shown in Fig. 1. The symbols + and − represent the positive and negative ions, respectively. A part of the ions are considered to be free, and another portion of the ions are in contact with each other, forming neutral molecules. The former were considered to conduct electricity and the latter to have no influence on the conductance of a solution. The positions of the ions and neutral molecules would, of course, be rapidly shifting, due to thermal vibrations. Neutral molecules were thought to be constantly break-

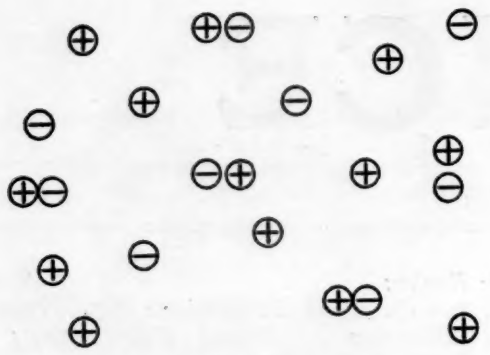

FIG. 1

ing up into ions and the ions, in turn, uniting to form molecules, the proportion of ions, however, increasing as the solution was made more and more dilute.

A large part of Arrhenius's theory can be summed up in the famous formula.

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \qquad (1)$$

in which $\alpha$ is the "degree of dissociation," that is to say, the fraction of the total electrolyte present as ions. In this formula $\Lambda$ is the conductance of a gram equivalent of the electrolyte and $\Lambda_\infty$ is the conductance of the same quantity of electrolyte at infinite dilution, under which condition the electrolyte is presumably completely dissociated. As will be discussed in more detail later, this equation involves the tacit assumption that the conducting properties, *i.e.*, the mobilities, of the ions, are the same at every dilution. A similar assumption was made by Arrhenius and later workers in dealing with the thermodynamic properties of the ions, which were also considered to be the same at all dilutions.

Although certain weaknesses were evident almost from the first, Arrhenius's theory held the field for several decades, and its reverberations in chemistry, physics and biology could hardly be traced in a lifetime of reading. In large measure the theory originated the borderland sciences of physical chemistry and biophysics. It is entitled to profound respect as one of the most useful stimulators of research that science has produced.

One of the early objections to the theory, represented by the statement that atoms of metallic sodium, for instance, could hardly remain in aqueous solution, was easily met by pointing out the fact that a charged sodium atom, to which molecules of solvent are probably attached, can be quite different from the metal. The other objection, that positive and negative ions can not remain in close proximity in solution without at least influencing each other, contains the real weakness of the Arrhenius theory. The great advances made recently in the theory of electrolytes, to be outlined in part in this paper, have all been in the direction of an attack on this vulnerable point.

Although Arrhenius's theory accounted quantitatively, with sufficient accuracy, for the behavior of "weak" electrolytes, *i.e.*, solutions of acids and bases which yield relatively poorly conducting solutions, the theory failed seriously when it was applied to highly conducting solutions. Thus computing the degree of dissociation with the aid of equation 1, it was found that for weak electrolytes the law of mass action held, for instance, for the equilibrium

$$HA \rightleftarrows H^+ + A^- \qquad (2)$$

where HA represents a weak acid, such as acetic acid. A large amount of ingenuity was expended in the attempt to explain the failure of strong electrolytes, such as sodium chloride, to fit into the same scheme. This and other related facts were lumped together as the "anomaly of the strong electrolyte," which plagued workers in this field for a full generation.

The most convenient method for measuring the thermodynamic properties of an electrolyte is, when applicable, to use it in a concentration cell. The simplest

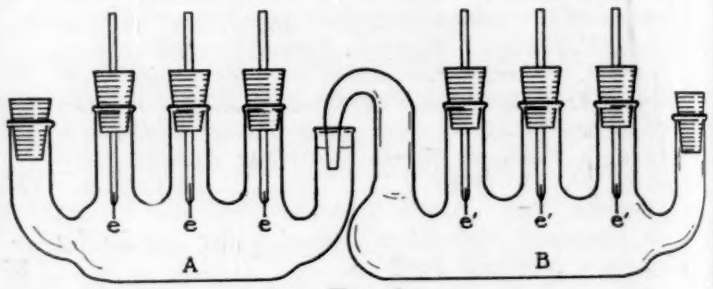


FIG. 2

type of such a cell is shown in Fig. 2. Here vessel A contains the more concentrated of two solutions, of sodium chloride, for example, and vessel B the more dilute. Into these solutions are placed electrodes (in this case silver covered with silver chloride), several being used for comparison. Such a concentration cell can be conveniently represented by the symbols

$$\begin{matrix} \text{Ag; AgCl, NaCl:} & \text{NaCl, AgCl; Ag.} \\ (C_A) & (C_B) \end{matrix} \qquad (3)$$

Now if the ions are "thermodynamically ideal" solutes the electromotive force, $E$, between electrodes in the two solutions should follow the equation

$$E = \frac{2t\,RT}{F} \log \frac{C_A \alpha_A}{C_B \alpha_B} \qquad (4)$$

in which $t$ is the transference number of the positive ion (*i.e.*, the proportion of the total conductance of the solution due to that ion), $R$ is the gas constant, $T$ the absolute temperature, and $F$ the faraday. $C_A$ and $C_B$ are the salt concentrations in vessels and A and B, respectively, of Fig. 2, and the degrees of dissociation $\alpha_A$ and $\alpha_B$ are computed from equation 1. Now it was part of the anomaly of strong electrolytes that this equation is very far from agreement with the actual

measurements. A way of sidetracking this difficulty and obtaining workable equations was suggested by G. N. Lewis. In effect he rewrote equation 4 as follows:

$$E = \frac{2t\,RT}{F} \log \frac{C_A f_A}{C_B f_B} \qquad (5)$$

The $f$ values used in this equation are obtained from the data and are called "activity coefficients." For a long time the $f$ values were purely empirical. They were, however, very useful since, if once determined, they could, with suitable precautions, be used in any thermodynamic equation. For moderately concentrated solutions these activity coefficients are less than unity but approach that value as a limit as the solutions become more and more dilute.

The rather remarkable assumption made by Arrhenius and his followers that charged ions could be present in solution without influencing each other's properties, remained almost unchallenged until Milner in 1912 and Debye and Hückel in 1923, in epoch-making papers, showed that the variation of the activity coefficients of ion constituents from unity can be explained by the electrostatic attractions and repulsions of the charges carried by the ions. Positive ions will attract negative ions, and *vice versa*. Due to heat vibrations of the ions themselves and of the solvent molecules, no regular arrangement of the ions persists, although it can be said that if you were taking a ride on one of the positive ions more of your neighbors would be negative ions than positive ones, and this would be more true the greater the concentration. Thus in a salt solution the ions are not quite independent of each other, and their thermodynamic properties would thus be expected to change with the concentration.

Using these simple assumptions and ingenious mathematical-physical reasoning, Debye and Hückel arrived at the formula

$$-\log f_i = \frac{A\sqrt{C}}{1 + Ba_i\sqrt{C}} \qquad (6)$$

in which $f_i$ is the ion activity cofficient, $A$ is a constant computable from universal constants, $B$ contains such constants and $a_i$ is the size of the ions, or more precisely speaking, the "distance of closest approach" of the positive and negative ions.

We have, at the Rockefeller Institute, made what we think are the most precise tests yet obtained of the Debye-Hückel theory, which has emerged with flying colors. Drs. A. S. Brown and Theodore Shedlovsky have measured the potentials of cells of the type represented by equation 3, and precision transference numbers have been obtained by Dr. L. G. Longsworth. These transference numbers are not, however, constants as assumed in obtaining equation 4, but are functions of the concentration $C$, which complicates the computation but not the theory. The actual equation used in the computations is

$$E = \frac{2\,RT}{F} \int_2^1 t\, d \log C f_i \qquad (7)$$

The results are represented in Fig. 3, where the negative of the logarithm of the activity coefficient is plotted against the square root of the concentration. The distance of closest approach, $a_i$, computed from the data is seen to vary from 5.6 Ångström units for

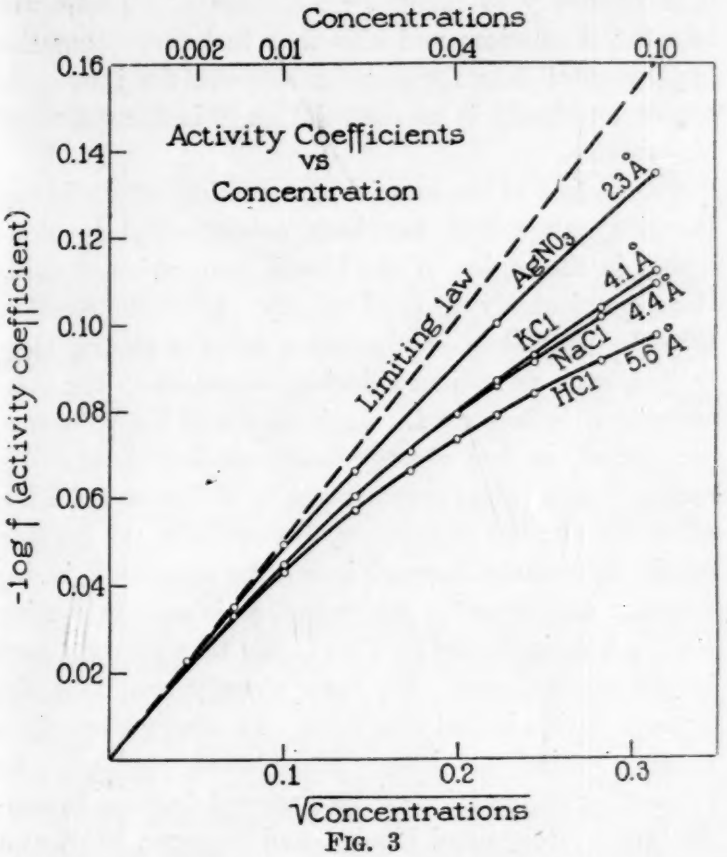


FIG. 3

hydrochloric acid to 2.3 Ångström units for silver nitrate. It will be seen from the plot that the agreement of observed and computed values is very close. As a matter of fact the agreement of the observed values of $f_i$ and those computed from equation 6 agree within a few hundredths of a per cent. up to a concentration of about 0.05 normal. It is evident that, for the substances mentioned, the new theory accounts adequately for the experimental results. If, as assumed in Arrhenius's theory, the ions had no influence on each other the activity coefficient, $f_i$, would be unity. This would correspond to the straight line forming the lower border of the diagram.[1]

[1] Fig. 3 also contains the straight line representing the "limiting law"

$$-\log f = A\sqrt{C}$$

which holds for exceedingly dilute solutions. It is not valid, as might be expected, for substances with very small distances of closest approach, since under those conditions the effects of certain approximations made in deriving equation 6 affect the computations. This matter has been investigated by Gronwall, LaMer and Sandved, *Physik. Z.*, 29: 358, 1928.

However, in obtaining equation 6 a very important simplifying assumption was made. Instead of postulating, as Arrhenius did, that the dissolved electrolyte is partly present as ions and partly as undissociated electrolyte it was found, for strong electrolytes at least, that agreement between theory and observation could be more readily obtained if it were assumed that the electrolyte is *all* present as ions. It was, somewhat unfortunately, this aspect of the theory that attracted most attention when it first appeared. It will be shown later in this paper that for "weak" electrolytes it is necessary to introduce a degree of dissociation into the discussion, and also that in interpreting the experimental data for these substances the interionic attraction theory is as essential as it is for "strong" electrolytes.

The success of the interionic attraction theory in the thermodynamic field has been accompanied by conquests in the region of the kinetic properties of solutions, particularly the conductivity. It will be recalled that the equivalent conductance, $\Lambda$, of a strong electrolyte, such as sodium chloride, decreases as the concentration is increased. Arrhenius and his followers considered, as has already been mentioned, this decrease of equivalent conductance to be due to a falling off in the number of carriers of electricity. A portion of the oppositely charged ions were supposed, in increasing degree as the concentration is raised, to stick together, as indicated in Fig. 1, and thus take no part in the conductance. We have already seen that the present notion is that a solution of a strong electrolyte consists entirely of ions. There must, obviously, be some other explanation of the observed decrease in conductance. Debye and Hückel, and Onsager, have, as a matter of fact, shown that there are two "effects" or mechanisms tending to bring about decreases in the equivalent conductance of an electrolyte with increase of concentration. Both of these arise from the attractions and repulsions of the charged ions. These are (a) the *electrophoretic effect* and (b) the time of *relaxation effect*. One of the consequences of the interionic attraction theory is that each ion carries around with it a so-called "ion atmosphere" due to considerations that have already been discussed. If a positive ion has, on the average, more negative than positive ions near it the result will be the same as if a charge of negative electricity were spread out symmetrically in all directions in the solvent, most of it lying near the chosen ion but spreading out more and more thinly as the distance from the ion increases. Although in the mathematical discussions of this potential it is treated as a reality, it is actually the result of a time average of a distribution of the ions, each ion serving both as a center of an ionic atmosphere and as a part of the ionic atmosphere of other ions. Now if a potential gradient is impressed on the solution, as in an electrolysis or a measurement of conductance, the charges of the ionic atmosphere will tend to move, carrying solvent with them, in a direction opposite to that of the chosen ion. This counter-current of solvent will impose a drag on the ion, tending to decrease its velocity. This is known as the "electrophoretic effect."

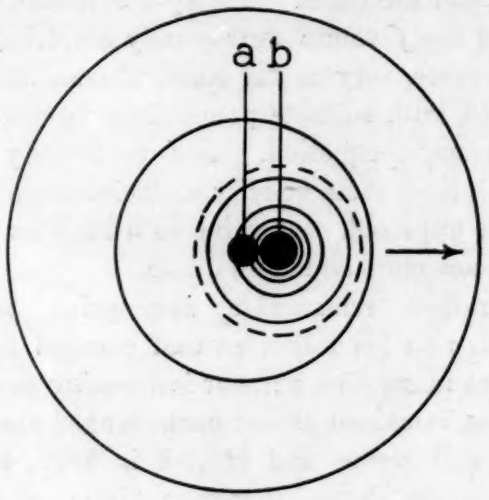


FIG. 4

The second effect is possibly more difficult to visualize, but an attempt is made in Fig. 4. If we move an ion, represented by the black circle, suddenly from position *a* to position *b* its "ionic atmosphere" will go along also in the same direction. However, it takes some time for a message that something has happened at the point where the ion is located to get to the outlying regions of the ion atmosphere. These un-notified regions (outside the dotted circle in the figure) are unsymmetrically spaced around the ion and thus exert a pull on the notified regions. This gives rise to an extra drag on the central ion. This picture gives a rough idea of the "time of relaxation effect."

The mathematical physics involved in the quantitative treatment of the electrophoretic and time of relaxation effects is formidable, but the final result, for binary electrolytes, such as potassium chloride or hydrochloric acid, is quite simple. The equation obtained by Onsager is

$$\Lambda = \Lambda_o - (\gamma \Lambda_o + \beta)\sqrt{C} \qquad (8)$$

in which $\Lambda$ and $\Lambda_o$ are respectively the measured and limiting conductances and $\gamma$ and $\beta$ are theoretical constants. Due to the complexity of the phenomena and of the mathematics this formula is valid only for very dilute solutions. A test of the equation has been furnished by the careful measurements made in the Rockefeller Institute laboratory by Dr. Shedlovsky. Some typical results are given in Fig. 5, in which equivalent conductance, $\Lambda$, values for sodium and potassium chlorides are plotted against the square root of the concentration. For comparison plots of the theoretical equation, 8, are represented as dotted lines. It will be seen

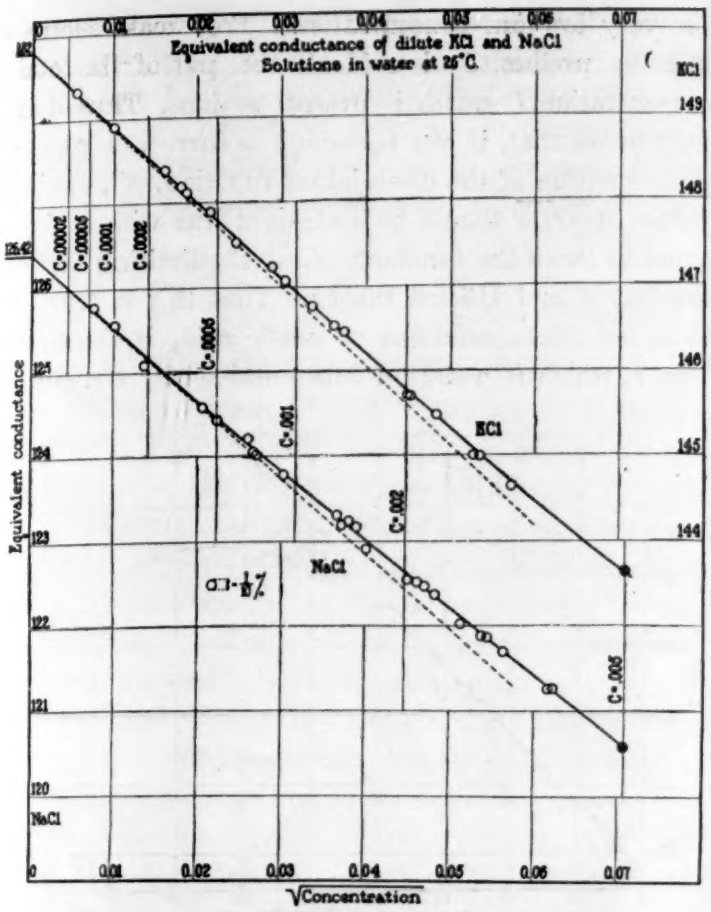


FIG. 5

that the equation represents the experimental results up to a concentration, $C$, of about 0.001, after which there are deviations which increase as the concentration increases. These deviations appear, however, to be such as would arise from the necessary simplifications used in obtaining the equation. Here again the assumption has been made that salts, such as sodium chloride, are entirely present as ions, *i.e.*, that they are completely dissociated.

There is an additional, and very sensitive, test that can be made of the newer conceptions. According to the theory of Arrhenius, the ions, being quite independent of each other, have the same mobilities at all concentrations, and, therefore, their transference numbers, which are the ratios of the mobility of one ion in a binary electrolyte to the sum of the mobilities of both ions, should remain constant. Modern developments in the Rockefeller Institute laboratory of the "method of moving boundaries" have made it possible to obtain transference numbers with about the same accuracy with which conductance can be measured. The transference number of, for instance, hydrogen ion in hydrochloric acid, $t_{H^+}$, is given by the relation

$$t_{H^+} = \frac{\lambda_{H^+}}{\lambda_{H^+} + \lambda_{Cl^-}} \qquad (9)$$

in which $\lambda_{H^+}$ and $\lambda_{Cl^-}$ are the mobilities of the hydrogen and chloride ions, respectively. If the Arrhenius theory were true this transference number should not change with the concentration. The interionic attraction theory, however, predicts that these transference numbers should vary and, furthermore, for very dilute solutions at least, how much they should change. Fig. 6 shows the results that have been obtained in

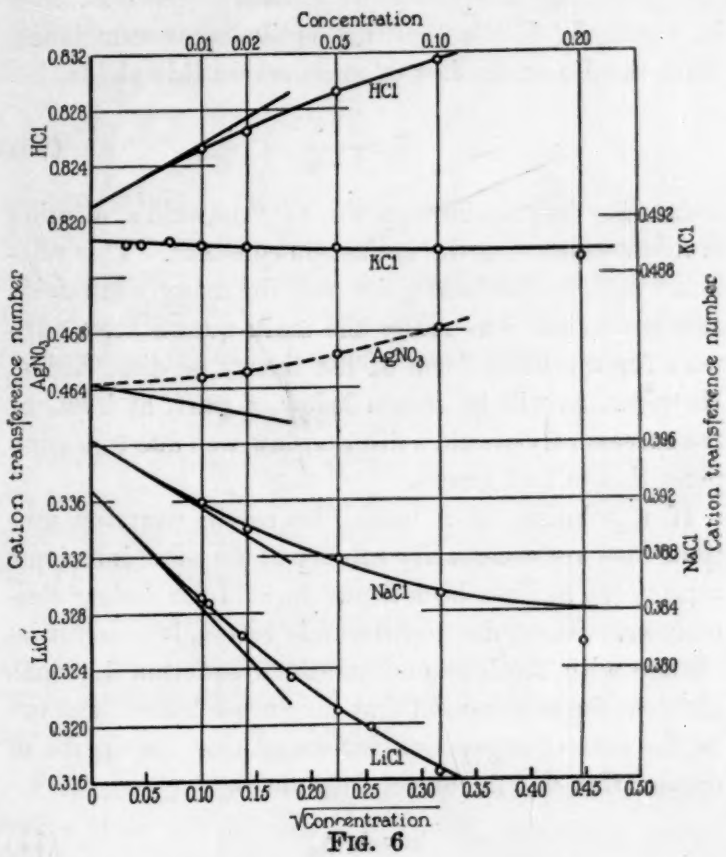


FIG. 6

this field by Dr. Longsworth. Here the measured transference numbers are plotted against the square root of the concentration and the curved lines have been drawn through these points. The change of the transference number predicted from Onsager's equation, 8, is represented in each case by the straight line starting from the value of the limiting transference number, at zero concentration. It will be seen that the curves passing through the observed points merge naturally into the theoretical line, with the exception of that for silver nitrate which substance is, in several respects, abnormal.

It is thus evident that the measurements of concentration cells, of conductances and transference numbers on strong electrolytes can all be readily interpreted by the new interionic attraction theory. It was in this region, of strong electrolytes, that the older Arrhenius theory was least successful.

There is, however, a large class, the so-called "weak" electrolytes, for which the assumption of complete dissociation is not adequate. For these there is evidence to indicate that the ions are in equilibrium with an appreciable concentration of undissociated electrolyte in agreement with Arrhenius's original picture. Such an equilibrium may be indicated by

$$HA \rightleftarrows H^+ + A^- \qquad (2)$$

in which HA represents a weak acid and $A^-$ the nega-

tive ion produced by its dissociation. As has already been mentioned, Arrhenius believed that the degree of dissociation, $\alpha$, could be computed from the relation

$$\alpha = \Lambda/\Lambda_\infty \qquad (1)$$

in which $\Lambda_\infty$ is the limiting equivalent conductance. With the aid of the law of mass action this yields

$$K = \frac{\alpha^2 C}{1-\alpha} \qquad (10)$$

a familiar expression known as "Ostwald's dilution law," in which $K$ is the ionization constant. This relation was found to hold quite well for many weak acids and bases, and was really the main quantitative support for the older form of the theory of dissociation. However, as will be shown below, a part, at least, of the success of Ostwald's dilution law was due to a compensation of two errors.

If a solution of a weak electrolyte contains ions these ions are necessarily subject to the same interionic attractions as have been found to hold for strong electrolytes. Since, due to interionic forces, ion mobilities change with the ion concentrations equation 1, which involves the assumption that they are constant, can not be the correct expression for computing the degree of dissociation $\alpha$. A correct formula is

$$\alpha = \Lambda/\Lambda_\varepsilon \qquad (11)$$

in which $\Lambda_\varepsilon$ is the equivalent conductance of the completely dissociated acid HA at the ion concentration $C\alpha$. The use of $\Lambda_\varepsilon$ instead of $\Lambda_\infty$ corrects for the electrophoretic and time of relaxation effects.[2] In addition, except at zero concentration, the ions are not, as we have seen, normal solutes, and thus have activity coefficients, $f_i$, generally less than unity. In modern terms, therefore, Ostwald's equation becomes

$$K = \frac{\alpha^2 C}{1-\alpha} \cdot f_i^2 = K' \cdot f_i^2 \qquad (12)$$

in which $\alpha$ is computed from equation 11 and $K'$, the "dissociation function" which is not in general constant, is defined by the equation. Equation 12 can be readily transformed into the expression

$$\log K = \log K' + 2 \log f_i = \log K' - 2A\sqrt{C\alpha} \qquad (13)$$

the last term coming from equation 6, which may be put into the form

$$-\log f_i = A\sqrt{C\alpha} \qquad (14)$$

[2] Values of $\Lambda_\varepsilon$ can be obtained as follows. The equivalent conductance $\Lambda_{\varepsilon(HAc)}$ of, for example, totally dissociated acetic acid may be obtained from the formula

$$\Lambda_{\varepsilon\,(HAc)} = \Lambda_{H^+Cl^-} + \Lambda_{Na^+Ac^-} - \Lambda_{Na^+Cl^-}$$

Each of the $\Lambda$ values on the right hand side of the equation must be determined for the concentration $C\alpha$. However, as $\alpha$ must be obtained from equation 11, a short series of trials or approximations must be made to establish the correct values.

for very low ion concentrations. For weak electrolytes the product $C\alpha$ is evidently the part of the total concentration $C$ which is present as ions. Thus it is easy to see that, if our reasoning is correct, a plot of the logarithm of the dissociation function, $K'$, against values of $\sqrt{C\alpha}$ should be a straight line with a slope equal to twice the constant, $A$, of the limiting law of the Debye and Hückel theory. That this is true, at least for dilute solutions of acetic acid, is shown in Fig. 7, which is based on data obtained by Dr. Shedlovsky. The solid line, $e$, has a slope of $2 \times 0.506$, the latter figure being the Debye-Hückel constant at 25°. The intercept of the straight line with the zero ordinate yields the thermodynamic ionization constant of acetic acid. This limiting value agrees almost exactly with a determination of the same constant made by Harned and Ehlers, using a method, depending upon the measurement of the potentials of concentration cells without liquid junctions, which involves none of the assumptions used in obtaining equation 13. A similar agreement between theory and observation has been obtained with chloroacetic and other acids. The reason why Ostwald's dilution law, equation 10, was moderately successful is now evident. Arrhenius's original expression, equation 1, yields degrees of dissociation, $\alpha$, which are too low. This error, from our present point of view, was more or less offset by the tacit assumption made by Arrhenius and Ostwald, that the activity coefficients are unity, whereas, for all dilute solutions at least, they are less than unity.

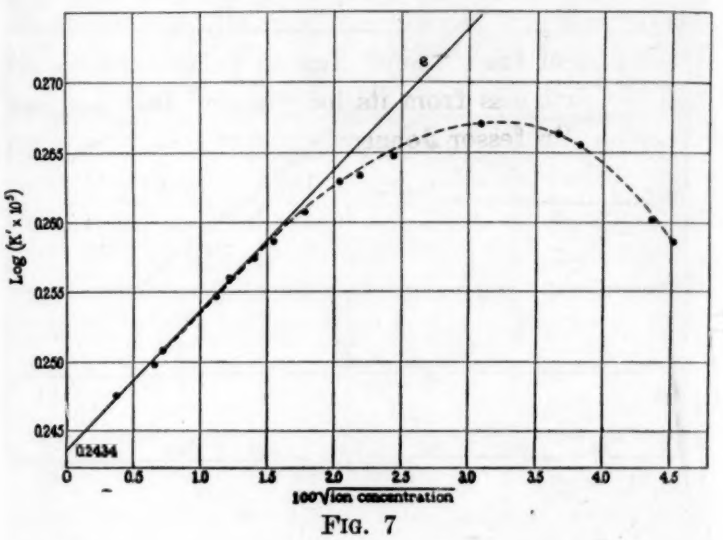

FIG. 7

This short survey of a large field has been confined to work done under the direction of the author at the Rockefeller Institute. A more complete discussion of the interionic attraction theory of electrolytes should include the researches at Columbia University, by Professor LaMer and associates, on electrolytes of higher valence types and on theoretical extensions of the Debye-Hückel theory; the researches of Professors Kraus and Fuoss at Brown University on solutions of

electrolytes in non-aqueous solvents; the work on the Wien and Debye-Falkenhagen effects, which deserve extended treatment, and many other researches that might be mentioned. In addition to clearing up a number of outstanding problems the new outlook has, as might be expected, raised quite a number of questions which demand investigation. However, enough of the theory has been outlined to show that it has been a useful tool of research and a powerful stimulator of investigation in what had become a somewhat stagnant field. Such stimulation of research is, of course, the main function of a theory.

# OBITUARY

## DUNCAN STARR JOHNSON[1]

IN the recent death, in the seventieth year of his age, of Duncan Starr Johnson, the Division of Biology and Agriculture of the National Research Council has suffered the first loss from its long list of distinguished chairmen. Professor Johnson spent practically all his active life as a scientist at the Johns Hopkins University, where at the time of his death he was professor of botany and director of the botanical garden.

Though his research lay largely in the field of plant morphology, with occasional excursions into ecology, he was singularly catholic in the breadth and accuracy of his knowledge of the field of plant science. Few men could have done what he did in conducting—at first single-handed, later with the cooperation of Professor Livingston—a department of botany of such distinction that graduate students were drawn from far and near, many of whom have taken honored places in American science.

As chairman of the Division of Biology and Agriculture for 1931–32, Professor Johnson showed the same characteristics that made him a great teacher. His most conspicuous qualities were an unswerving integrity and independence and a devotion to accuracy that sometimes seemed almost extreme. Duty to him was a sacred word, and he followed his ideals without a trace of compromise. To him and to men like him American science owes much. The Division of Biology and Agriculture mourns his loss as a friend, as an exemplar of the true scientific spirit and as one who served it with scrupulous regard to his obligations as chairman.

## RECENT DEATHS

FRANK TWEEDY, topographer and topographical engineer to the U. S. Geological Survey from 1884 until his retirement in 1926, died on June 28 at the age of eighty-three years.

LEON CHESTER MARSTON, JR., who was recently appointed assistant professor of entomology at Pennsylvania State College, died on June 22. He was thirty-two years old.

A CORRESPONDENT writes: "Paul Vere Roundy died suddenly at his home on June 21, following many months of ill health. He was born in 1884 and was appointed a member of the U. S. Geological Survey in 1908. In the ensuing twenty-eight years he served as geologist and paleontologist, working especially in the oil fields of Oklahoma and of California and in the phosphate reserve of Florida. He was also known through his work on the ostracods and conodonts, which was interrupted by his untimely death in his fifty-third year."

# SCIENTIFIC EVENTS

## ACTIVITIES OF THE INTERNATIONAL UNION OF BIOLOGICAL SCIENCES

IN the Executive Committee of the International Union of Biological Societies the following changes have been necessary: Professor Sir Albert Seward, our eminent president for the last period, not being reeligible, has been succeeded by Professor E. D. Merrill, of Harvard University; the vice-president, Professor Godlewski, by Professor D. M. S. Watson, of London, and the general secretary, Professor de Selys Longchamps, who has retired, by the undersigned. We have to thank most cordially Professor Seward for the very able way in which he conducted the work on behalf of our union and Professors Godlewski and de Selys for their activity.

In addition to the countries which had already joined the union (The Argentine, Belgium, Czechoslovakia, France, Great Britain, Italy, Japan, Jugoslavia, Morocco, the Netherlands, Poland, Portugal, South Africa, Spain and Switzerland) we were much pleased in welcoming Sweden and the United States of America; negotiations with a number of other countries have not yet been concluded.

The union granted subventions to the Central Bureau for Fungus Cultures at Baarn, to the Concilium Bibliographicum at Zurich, to the International Office for Nature Protection at Brussels and to the Année Biologique at Paris; it subscribed to the *Zoological Record*, London.

[1] Memorial adopted by the Division of Biology and Agriculture of the National Research Council on April 24, 1937.

A General Assembly was held at Amsterdam from September 1 to 5, 1935, at the time of the sixth International Botanical Congress. The chief points of discussion for this assembly have been a reorganization of the union, which has been confirmed in its new statutes and the establishment of a connecting link between the international botanical congresses and the union.

The revision of the statutes enabled both the botanical and zoological sections of the union to obtain a more independent existence, which has resulted in a revival of the botanical section, now put under the charge of its new secretary, Dr. Verdoorn.

A further point of discussion has been the question of exact accuracy with regard to dates of publications in order to forestall disputes as to priority. It has been agreed that the date of receipt of a manuscript should be given under the title and the date of final printing at the end of the paper, the final date of publication being accepted for priority.

Papers were read by Dr. S. J. Wellensiek, Buitenzorg, Java, on "The Publication of Botanical Work," and by Professor H. Humbert, Paris, on "Sur la Protection de la Nature, considérée du point de vue biologique, dans les pays tropicaux et subtropicaux."

The report of this assembly was published by the union in March, 1936, and copies of it may be obtained from the general secretary.

The next General Assembly probably will be held in July, 1940, at Stockholm, immediately before the seventh International Botanical Congress.

M. J. SIRKS,
*General Secretary*

WAGENINGEN, NETHERLANDS

## AWARDS FOR EXHIBITS AT THE ATLANTIC CITY MEETING OF THE AMERICAN MEDICAL ASSOCIATION

THE report of the Committee on Awards for exhibits presented at the Atlantic City meeting is given in the *Journal* of the American Medical Association.

Awards in Class I made for exhibits of individual investigation, which are judged on the basis of originality and excellence of presentation, were as follows:

**The Gold Medal to Leonard G. Rowntree, Arthur Stenberg, N. H. Einhorn, J. H. Clark, George M. Dorrance and E. F. Ciccone, Philadelphia Institute for Medical Research, Laboratory of Philadelphia General Hospital and American Oncologic Hospital, Philadelphia, and A. M. Hanson, Faribault, Minn., for an exhibit illustrating an original investigation on normal and abnormal growth associated with the development of sarcoma in albino rats from the ingestion of a crude wheat germ oil made by ether extraction.**

**The Silver Medal to Eben J. Carey, department of anatomy, Marquette University School of Medicine, Milwaukee, for an exhibit illustrating original investigation on intrinsic wave mechanics of the nervous and muscular systems.**

**The Bronze Medal to Louis Gross, Mount Sinai Hospital, New York, for an exhibit illustrating experimental studies of the blood supply to the heart in relation to coronary sclerosis.**

Certificates of Merit, Class I, are awarded to the following (alphabetically arranged):

**Lester R. Dragstedt and John Van Prohaska, department of surgery, University of Chicago Clinics, for exhibit of original work on lipocaic, a new pancreas hormone.**

**Harry Goldblatt, department of pathology, Western Reserve University School of Medicine, for an exhibit illustrating results of work on experimental hypertension.**

**Nelse F. Ockerblad and Hjalmar E. Carlson, department of urology, University of Kansas School of Medicine, for an exhibit illustrating the distribution of urethral pain.**

**Isaac Schour, University of Illinois, Chicago, for an exhibit illustrating tooth-ring analysis.**

**Charles S. Venable, Walter G. Stuck and Asa Beach, San Antonio, Texas, for an exhibit illustrating the effect of electrolysis in osteosynthesis with metals.**

In addition, the following exhibits are deemed worthy of honorable mention (alphabetically arranged):

**Elmer L. De Gowin and W. L. Randall, department of internal medicine, State University of Iowa, on renal damage from blood transfusion.**

**Deryl Hart, Duke Hospital, Durham, N. C., on sterilization of the air in the operating room with bactericidal radiant energy.**

**Herbert L. Johnson, Boston, illustrating absorbable sutures and insulating patches made from human and bovine fetal membranes.**

**Virgil H. Moon, David R. Morgan and Marshall M. Lieber, department of pathology, Jefferson Medical College, Philadelphia, illustrating shock, its pathology and sequelae.**

**J. W. Schereschewsky, United States Public Health Service and Harvard Medical School, Boston, on carcinogenic compounds and lung tumors in mice.**

**Marvin R. Thompson, University of Maryland, on ergot and its active principles.**

**W. F. Wells and Mildred Weeks Wells, Harvard School of Public Health, Boston, on air-borne infection.**

Particular commendation is made of the personal demonstration by Edward C. Rosenow, Mayo Foundation, Rochester, Minn., of his exhibit on the relation of streptococci to the viruses of encephalitis and poliomyelitis.

## THE ROCHESTER MEETING OF THE AMERICAN CHEMICAL SOCIETY

THE next meeting of the American Chemical Society will be held at Rochester, N. Y., on September

11 and 12. The honorary chairman of the local committee in charge of arrangements is Florus R. Baxter, formerly head of the laboratories of the Vacuum Oil Company; the general chairman is M. H. Eisenhart, of the Bausch and Lomb Optical Company, and the secretary is Dr. Earle M. Billings, of the Eastman Kodak Company.

The society will meet in seventeen divisions. These, with the names and addresses of the secretary of each, are as follows:

*Agricultural and Food Chemistry.* G. A. Fitzgerald, The Birdseye Laboratories, 3 Commercial St., Boston, Mass.

*Biological Chemistry.* W. C. Russell, Agricultural Experiment Station, New Brunswick, N. J.

*Cellulose Chemistry.* W. O. Kenyon, Research Laboratory, Eastman Kodak Co., Rochester, N. Y.

*Chemical Education.* N. W. Rakestraw, department of chemistry, Brown University, Providence, R. I.

*Colloid Chemistry.* L. H. Reyerson, Chemistry Bldg., University of Minnesota, Minneapolis, Minn.

*Fertilizer Chemistry.* H. C. Moore, P. O. Box 1685, Atlanta, Ga.

*Gas and Fuel Chemistry.* Alden H. Emery, Room 728, Mills Bldg., Washington, D. C.

*History of Chemistry.* Mildred W. Grafflin, *Chemical Abstracts,* Ohio State University, Columbus, Ohio.

*Industrial and Engineering Chemistry.* Assistant Secretary, Howard S. Gardner, M. I. T. Station, Eastern Manufacturing Co., Bangor, Maine.

*Medicinal Chemistry.* W. H. Hartung, School of Pharmacy, University of Maryland, Baltimore, Md.

*Microchemical Section.* Walter R. Kirner, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

*Organic Chemistry.* Ralph L. Shriner, Department of Chemistry, University of Illinois, Urbana, Ill.

*Paint and Varnish Chemistry.* G. G. Sward, 2201 New York Ave., N. W., Washington, D. C.

*Petroleum Chemistry.* C. R. Wagner, Pure Oil Co., 35 East Wacker Drive, Chicago, Ill.

*Physical and Inorganic Chemistry.* George Scatchard, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

*Rubber Chemistry.* C. W. Christensen, Rubber Service Laboratories Co., 1012 Second National Bldg., Akron, Ohio.

*Sugar Chemistry.* E. W. Rice, National Sugar Refining Co. of New Jersey, 129 Front St., New York, N. Y.

*Water, Sewage and Sanitation Chemistry.* C. R. Hoover, 8 Pike Place, Middletown, Conn.

The only division that has not planned for a program at Rochester is that of oil and gelatin.

Titles for papers, which should be sent to the secretary of the appropriate division, must be received not later than July 14.

## OFFICERS OF THE AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS

W. H. HARRISON, assistant vice-president of the department of engineering and operation of the American Telephone and Telegraph Company, New York, N. Y., was elected president of the American Institute of Electrical Engineers for the year beginning on August 1, at the annual meeting held in Milwaukee, Wis., during the annual summer convention of the institute. The other officers elected were: *Vice-presidents,* I. Melville Stein, Philadelphia, Pa.; Edwin D. Wood, Louisville, Ky.; L. N. McClellan, Denver, Colo.; J. P. Jollyman, San Francisco, Calif.; M. J. McHenry, Toronto, Canada. *Directors,* C. R. Beardsley, Brooklyn, N. Y.; V. Bush, Cambridge, Mass.; F. H. Lane, Chicago, Ill. *National Treasurer,* W. I. Slichter, New York, N. Y. (reelected).

These officers together with the following hold-over officers will constitute the Board of Directors for the next administrative year, beginning on August 1: A. M. MacCutcheon (retiring president), Cleveland; O. B. Blackwell, New York; L. T. Blaisdell, Dallas, Tex.; F. M. Farmer, New York; N. E. Funk, Philadelphia; H. B. Gear, Chicago, Ill.; C. Francis Harding, Lafayette, Ind.; F. Ellis Johnson, Columbia, Mo.; C. R. Jones, New York; W. B. Kouwenhoven, Baltimore; K. B. McEachron, Pittsfield, Mass.; C. A. Powel, East Pittsburgh; C. E. Rogers, Seattle; R. W. Sorensen, Pasadena; A. C. Stevens, Schenectady; J. B. Whitehead, Baltimore.

The annual report of the Board of Directors, presented at the meeting, showed a total membership on April 30 of 15,308. In addition to two national conventions and two district meetings, 1,984 meetings were held during the year by the local organizations of the institute in the principal cities and educational institutions in the United States, Canada and Mexico.

## AWARD OF THE LAMME MEDAL OF THE SOCIETY FOR THE PROMOTION OF ENGINEERING EDUCATION

DEAN FREDERICK E. TURNEAURE, of the College of Engineering of the University of Wisconsin, was awarded the Lamme Medal, bestowed for outstanding accomplishment in the advancement of the art of technical training, at the forty-fifth annual dinner on July 1 of the Society for the Promotion of Engineering Education at the Massachusetts Institute of Technology.

Dean Turneaure received the medal, in the presence of nearly a thousand members of the society, from Dr. E. B. Roberts, chairman of the Committee on the Lamme Medal Award, who announced that Dean Turneaure was chosen as recipient of the tenth Lamme

Medal "for his influence upon the policies and people of the College of Engineering of the University of Wisconsin; for his conception of a university as a cooperative enterprise of scholars and disciples in which freedom and power to initiate is diffused, not centralized; for the spirit of steadiness and confidence he has engendered; for the harmonious and cooperative relations within faculty and between faculty and students that have matured under his leadership; and in recognition of the high place he has filled in engineering education and in public estimation not only in his commonwealth but in the nation as well."

The Lamme Medal was established under the will of Benjamin G. Lamme, chief engineer of the Westinghouse Electric and Manufacturing Company, who died in 1924, to be awarded annually to a technical teacher for accomplishment in technical teaching or actual advancement of the art of technical training.

Dean Turneaure was born on a farm near Freeport, Ill., on July 30, 1866. He was graduated in civil engineering at Cornell University in 1889, and immediately engaged in railway engineering work. In 1890 he became an instructor in civil engineering at Washington University in St. Louis, and in 1892 he was appointed professor of bridge and hydraulic engineering at the University of Wisconsin. In 1902 he was appointed acting dean and in 1904 dean of the College of Mechanics and Engineering of the university, and director of the Engineering Experiment Station.

Dean Turneaure served as city engineer for Madison, Wisconsin, for 1900–02. He has been chairman of the Wisconsin Registration Board of Architects and Professional Engineers since 1932; he has served as president of the Society for the Promotion of Engineering Education in 1908–09, and was a member of the Board of Investigation and Coordination which directed the comprehensive study of engineering education carried out by the society from 1923 to 1929. He has conducted pioneer experimental and analytical investigations on impact and secondary stresses in bridges under moving train loads, and also on the strength of steel columns.

# SCIENTIFIC NOTES AND NEWS

DR. ROBERT A. MILLIKAN, who was unable to attend the medal meeting of the Franklin Institute on May 18, received the Franklin gold medal and certificate of honorary membership in the Franklin Institute after his return from Europe on June 25. The medal was awarded "in recognition of his isolation and measurement of the fundamental unit of electricity, the electron; the photo-electric determination of the fundamental constant of radiation, Planck's constant; the extension of the ultra-violet spectrum by two octaves to join the spectrum of the soft x-rays, and the study of the nature and properties of a very penetrating radiation of cosmic origin."

DR. JOEL H. HILDEBRAND, professor of chemistry at the University of California, has been elected a corresponding member of the Physico-Medical Society of the University of Erlangen, "in recognition of his scientific services in the region lying between physical and organic chemistry and in furtherance of personal relationships between the scholars of the world."

DR. MOSES GOMBERG, professor emeritus of organic chemistry, received the degree of doctor of laws at the commencement exercises of the University of Michigan.

SIR FREDERICK GOWLAND HOPKINS, Sir William Dunn professor of biochemistry at the University of Cambridge, recently president of the Royal Society, has been elected president of the Association of Scientific Workers. This organization was founded with the name of the Science Guild by Sir Norman Lockyer in 1918, its object being "to secure wider applications of science and scientific methods for the welfare of society and advance the professional interests of scientific workers."

DR. RICHARD HESSE, professor of zoology at the University of Berlin, has been made an honorary member of the Bavarian Academy of Sciences.

THE Henry Russell award of $250 of the University of Michigan "to an assistant professor or instructor whose research and scholarly activities show the greatest promise" has been given to Dr. Frank E. Eggleton, assistant professor of zoology. The Henry Russell lecturer, who was named earlier in the year, is Dr. Charles W. Edmunds, chairman of the department of materia medica and therapeutics of the Medical School.

THE Explorers Club and the American Russian Institute for Cultural Relations with the Soviet Union gave a dinner on June 30 in honor of the Soviet transpolar flyers, Valeri Chkalov, Georgi Baidukov and Alexander Beliakov, at the Waldorf-Astoria Hotel, New York City. Dr. Vilhjalmur Stefansson presided, and Lowell Thomas was toastmaster.

THE Ward Burdick Award for 1937 of the American Society of Clinical Pathologists has been made to Dr. Stanley P. Reimann, of the Lankenau Institute of Cancer Research, Philadelphia, for his work on cancer research. Dr. Henry F. Hunt, of Danville, Pa., was awarded the gold medal for his exhibit on the etiology of eclampsia, and Dr. B. Steinberg, of Toledo, Ohio,

was awarded the silver medal for his exhibit on the etiology and treatment of acute peritonitis. The following officers were elected: *President-elect,* Dr. T. B. Magath, Rochester, Minn.; *Vice-president,* Dr. S. P. Reimann, Philadelphia; *Executive Committee,* Dr. R. R. Kracke, Emory University, Ga.; Dr. L. C. Todd, Charlotte, N. C.; *Board of Censors,* Dr. H. R. Prentice, Kalamazoo, Mich.; Dr. H. L. Reinhart, Columbus, Ohio; *Board of Registry,* Dr. I. Davidsohn, Chicago; Dr. A. Yaguda, Newark, N. J.

THE American Society for Testing Materials has elected the following officers for 1937–1938: *President* (one year), Dr. A. E. White, professor of metallurgical engineering and director of the department of engineering research, University of Michigan; *Vice-president* (two years), H. H. Morgan, manager, Rail and Track Fastenings Department, Robert W. Hunt Company, Chicago; *Members of Executive Committee* (two years), P. H. Bates, chief of the Clay and Silicate Products Division of the National Bureau of Standards; H. F. Clemmer, engineer of materials, District of Columbia; Dr. G. E. F. Lundell, assistant chief of the Division of Chemistry of the National Bureau of Standards; H. C. Mougey, chief chemist and assistant technical director, Research Laboratories Division of the General Motors Corporation, and R. L. Templin, chief engineer of tests, Aluminum Company of America.

DR. WILTON M. KROGMAN, associate professor of physical anthropology and anatomy at Western Reserve University, has been elected president of the Central Section of the American Anthropological Association.

DR. ULYSSES P. HEDRICK, director of the New York State Agricultural Experiment Station at Geneva, N. Y., presented his resignation to the Board of Trustees of Cornell University on June 28. The resignation will take place on January 15, his sixty-eighth birthday, when he will have reached the age limit. Dr. Hedrick became horticulturist at the station in 1905 and was appointed director in 1928.

DR. GEORGE PERKINS CLINTON, for thirty-five years botanist at the Agricultural Experiment Station at New Haven, Conn., has retired, but, as consulting botanist, will continue to work at the station.

DR. HENRY B. KUMMEL retired on July 1 as state geologist of New Jersey and director of the Department of Conservation and Development. He will serve as consulting geologist at a salary of $4,500 a year. Dr. Kummel, who has been in the service of the state for more than forty years, will be succeeded as director of the department by State Forester Charles P. Wilber, whose salary will be increased, it is reported, from $5,800 to $7,500. Meredith E. Johnson, who has been assistant geologist, becomes state geologist at a salary of $4,800 instead of his present salary of $4,200.

RETIRING members of the faculty of Princeton University include Dr. Lauder W. Jones, Hepburn professor of organic chemistry, formerly chairman of the department of chemistry, and Malcolm MacLaren, professor of electrical engineering.

DR. JOHN E. GORDON, of Chicago, now field director of the International Health Division of the Rockefeller Foundation, has been appointed professor of preventive medicine and epidemiology at the Harvard Medical School.

DR. R. V. BOUCHER, formerly national research fellow at Yale University and recently nutrition specialist for the American Can Company, has succeeded Dr. J. E. Hunter as research professor in poultry nutrition in the department of agricultural biochemistry at the Pennsylvania State College.

CARL C. MONRAD, for the past seven years chemical engineer in the Research Department of the Standard Oil Company of Indiana at Whiting, has been appointed associate professor of chemical engineering at the Carnegie Institute of Technology.

OTTO G. JENSEN has resigned from the research staff of the General Foods Corporation, Battle Creek, Mich., and has joined the staff of the Research Division of the Borden Company, Bainbridge, N. Y.

DR. HOWARD A. SMITH, until recently connected with an investigation for the Chemical Foundation of pit corrosion of stainless steel at the Massachusetts Institute of Technology, has been placed in charge of the corrosion and high temperature oxidation work at the Metallurgical Laboratory of the Republic Steel Corporation at Canton, Ohio.

DR. W. C. LOWDERMILK was recently appointed chief of the Division of Research of the Soil Conservation Service, not chief of the service, as erroneously reported in SCIENCE.

DR. H. L. RICHARDSON, of the department of chemistry at the Rothamsted Experimental Station, Harpenden, England, has been appointed adviser in soils and fertilizers to the National Agricultural Research Bureau, Shaolingwei, Nanking, China.

A SURVEY of how radio, sound recording and reproduction, motion pictures, photography and other scientific achievements may be applied to promotion of learning is to be conducted by a special committee of the National Research Council. Irvin Stewart, vice-chairman of the Federal Communications Commission, has been appointed director. Dr. James B. Conant, president of Harvard University, is chairman of the

committee, which will establish offices in New York City and appoint experts and consultants to aid in its inquiries. Members of the committee in addition to Dr. Conant are Dr. Vannevar Bush, vice-president of the Massachusetts Institute of Technology; Dr. L. D. Coffman, president of the University of Minnesota; Dr. Frank B. Jewett, president of the Bell Telephone Laboratories; Professor Ben D. Wood, of Columbia University; Dr. B. M. Webster, and Dr. Ludvig Hektoen, director of the John McCormick Institute for Infectious Diseases at the University of Chicago.

THE Committee on Scientific Research of the American Medical Association has made a grant to the Medical Department of the University of Rochester School of Medicine and Dentistry for work dealing with antiserum for white blood cells to be carried out under the direction of Dr. John S. Lawrence. A further grant has been made to support the research of Dr. J. C. Davis, of Minneapolis, on the effects of various drugs upon the coronary circulation in the heart lung preparations and in the intact heart. A grant has also been made to Dr. Walter A. Bloedorn, clinical instructor in medicine and acting dean of the Medical School of the George Washington University, to carry on his work on the effect of sodium pyruvate and other substances on Vitamin B deficiency.

PROFESSOR L. E. MELCHERS, head of the department of botany and plant pathology of the Kansas State College, gave the annual lecture before the Nebraska Academy of Science on the evening of May 7. He spoke on "Life and Scenes along the Nile." Professor Melchers was chief mycologist for the Egyptian Ministry of Agriculture at Cairo in 1927-1929.

THE Smith Chapter of the Society of the Sigma Xi held its annual initiation exercises on April 29. Two members of the faculty and seventeen students were initiated. Fordyce Tuttle, of the Eastman Kodak Company, spoke on "Problems Which Make the Design of Motion Picture Apparatus Interesting." Newly elected officers of the chapter are: Dr. Jessie Y. Cann, *president;* Dr. Myra M. Sampson, *vice-president;* Dr. Lois T. Slocum, *secretary,* and Dr. Deane Montgomery, *treasurer.*

SIGMA PI SIGMA, physics honor society, on June 15 installed its thirty-third chapter at the Washington Square College of New York University. The installing officer was Dr. Marsh W. White, of the Pennsylvania State College. Dr. H. C. Rentschler, director of the Westinghouse Research Laboratory, Bloomfield, New Jersey, was received into the society as an honorary member following the installation and spoke at the first open meeting of the chapter that evening on the subject, "Recent Developments in Photoelectricity."

THE International Congress of Psychology, which was to have been held in Madrid in September, 1936, but which was postponed owing to the Spanish war situation, will meet in the Sorbonne, Paris, from July 25 to 31; M. Yvon Beldos, French minister of foreign affairs, will declare the congress open on Sunday. Professor Pierre Janet is honorary president and Professor Henri Piéron is president of the committee of organization. Members of the International Executive Committee are: Professor Ed. Claparède, the University of Geneva; Professor Herbert S. Langfeld, Princeton University; Dr. C. S. Myers, National Institute of Industrial Psychology, London; Dr. Henri Piéron, Paris; Dr. Mario Ponzo, Rome; Dr. L. William Stern, Duke University, formerly of the University of Hamburg, and Dr. Edgar Rubin, University of Copenhagen.

THE fifth International Congress of Radiology will take place in Chicago from September 13 to 17, under the presidency of Dr. Arthur C. Christie, of Washington, D. C. The unity of medicine will be the main theme of the congress, with emphasis on the integral place of radiology in diagnosis and treatment.

THE Pan American Medical Association has made public the itinerary for its seventh cruise-congress, beginning with departure of delegates from New York aboard the Furness Bermuda liner *Queen of Bermuda* on January 15, returning on January 31. The cruise will touch Havana, Port au Prince, Trujillo City and San Juan. The main part of the congress will be held in Havana. There will be three days of scientific sessions with operative clinics. Special sections will be held on tuberculosis, gastro-enteritis, dentistry and industrial medicine.

THE Association for the Study of Internal Secretions, at its recent annual meeting, approved the monthly publication of its journal, *Endocrinology,* in two volumes per year, beginning in January, 1938. This expansion is intended to increase the facilities for and to expedite the publication of original endocrine research.

UNDER the will of the late George Weems Williams his estate is held in trust for Mrs. Williams and his brothers and sisters. On their death the Johns Hopkins Hospital will receive about $400,000.

A GIFT of two thousand acres of land to the Commonwealth of Massachusetts has been made by Bradley W. Palmer, of the law firm of Palmer, Dodge, Barstow, Wilkins and Davis. The property is situated in Ipswich and Topsfield—1,600 acres of it on the east side of the Newburyport Turnpike and 400 acres on the west side. Under the name of Willow Dale State Forest, part of it is to be maintained as a wildlife sanctuary and the remainder as a forest.

# DISCUSSION

## THE CHEMICAL NATURE OF "ASCORBIC ACID OXIDASE"[1]

As part of a general program of studies on the possible reactions of vitamin C in tissues, we have been interested in the various "enzymes" reported as occurring in plant juices that catalyze aerobic oxidation of the vitamin. If there were one or more widely distributed enzymes that served in a specific manner for the reversible oxidation of vitamin C, such evidence would have a strong bearing upon the postulated function of the vitamin in tissue respiration.

All our evidence, however, points toward a simpler interpretation of the observed phenomena and lends greater significance to the work of Barron and associates in emphasizing the rôle of copper as a catalyst for the aerobic oxidation of vitamin C. In addition to the physiological implications, the results are important in relation to methods of vitamin analysis and methods of vitamin preservation.

A detailed report will appear in another publication, but in view of the general interest of the problem for non-chemists and chemists, a brief summary of the evidence may be stated as follows:

(a) The copper content of the "enzymes" from squash and cauliflower is sufficient to account for the observed catalysis, and the greater part of the Cu in such preparations is found in the coagulated protein upon heat inactivation; (b) mixtures of copper salts with albumin exhibit properties like those of the postulated "enzymes" with respect to catalysis, inhibition, heat and acid inactivation, optimum pH and stability; (c) seven different copper inhibitors, both organic and inorganic, have the same relative effects upon pure copper compounds, copper-protein mixtures and the "enzymes"; (d) copper biuret exhibits a catalytic effect that is equivalent, atom per atom, to that of simple copper salts.

Although the above findings for plant tissue extracts suggest a possible relationship between the vitamin and copper in the living organism, there is not sufficient evidence to establish such a view-point at the present time. We do suggest, however, that there is no further need for using such terms as "ascorbic acid oxidase," "vitamin C oxidase" and "hexuronic acid oxidase" in the literature, at least in the sense that they have been used in the past.

ELMER H. STOTZ,
CARTER J. HARRER,
*Buhl Foundation Research fellows*
C. G. KING

[1] Journal publication 338 from the Chemistry Department, University of Pittsburgh.

## THE SELENIUM DEHYDROGENATION OF α-TOCOPHEROL

EVANS, Emerson and Emerson[1] isolated from wheat germ oil a substance with vitamin E-like properties which they named α-tocopherol. This product was a light-colored oily alcohol, showing a characteristic absorption band at 2980 Å., $E^{1\%}_{1cm.} = 90$ ca. Analyses of both the p-nitrophenyl urethane and the allophanate indicated a provisional formula of $C_{29}H_{50}O_2$.

Previous observations concerning vitamin E concentrates prepared from wheat germ oil and cottonseed oil suggested that the vitamin probably belonged to either the steroids or the triterpenoid alcohols.[2]

In an attempt to advance the knowledge with regard to the structural nature of vitamin E, two samples of α-tocopherol were subjected to dehydrogenation by means of selenium at a temperature of 300°–330°. In both experiments, the resulting mixture consisted of a volatile crystalline fraction and a fluorescent oily fraction. Purification of the volatile material by sublimation and recrystallization from dilute ethanol yielded light yellow, needle-shaped crystals having a melting point of 106°. A comparison of the physical and chemical properties of these crystals with an authentic sample of duroquinone indicated that the substance was duroquinone.

An analysis of the purified crystalline product obtained by the selenium dehydrogenation of α-tocopherol was performed by Dr. Helen Stantial, of the University of Toronto, who kindly supplied the following data:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Calculated for $C_{10}H_{12}O_2$ | | C | 73.13 | H | 7.37 | O | 19.49 |
| Found | I | C | 72.76 | H | 7.34 | O | 19.90 |
| | II | C | 72.97 | H | 7.58 | O | 19.45 |
| Mean | | C | 72.87 | H | 7.46 | O | 19.68 |

It is suggested that this fraction represents a cleaved side-chain from the α-tocopherol molecule and that the side-chain probably consists of two isoprene units. The fluorescent oily fraction is being investigated with a view to determining the nuclear structure of the alcohol.[3]

C. S. MCARTHUR
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MEDICAL SCHOOL

## INFERIOR YIELDS OBTAINED FROM CROSSES OF SIX-ROWED WITH TWO-ROWED BARLEYS

OUR cultivated barleys, so far as we know, all contain 7 (haploid) chromosomes. The morphological variation is enormous. In the 6-rowed group all three

[1] H. M. Evans, O. H. Emerson and G. A. Emerson, *Jour. Biol. Chem.*, 113: 319, 1936.
[2] F. A. Askew, *Biochem. Jour.*, 29: 472, 1935.
[3] MS. received May 15, 1937.

spikelets at a node of the rachis produce one fertile flower each. In the 2-rowed group the lateral spikelets are sterile and only a single seed is produced at each node. Crosses are easily made between the two groups, and there is no evidence of sterility nor of incompatibility in their appearance. Our recent results indicate that the ease of hybridization and the complete fertility in such crosses may not tell the whole story. The 2-rowed × 6-rowed crosses are inferior in yield to either 6-rowed × 6-rowed or 2-rowed × 2-rowed. This was definitely shown in an elaborate experiment in which essentially all the 378 combinations were made between 28 parents. There were included in the test 149 crosses of 6-rowed on 2-rowed and 209 crosses of 6-rowed on 6-rowed. In 1935, 2,921 selections were made from the 378 crosses. In the years before selections were made the yields of the 6-rowed × 2-rowed crosses were decidedly lower. In 1936 the average yield of the selections from 6-rowed × 2-rowed was only 89 per cent. of that of the 6-rowed × 6-rowed crosses. This percentage would not be so striking were it not for the large numbers involved. There were 1,789 selections of 6-rowed × 6-rowed and 961 of 6-rowed × 2-rowed. Out of the 1,789, 757, or 42.3 per cent., were worthy of further trial, while only 167, or 17.5 per cent., were continued from the 961 selections from 6-rowed × 2-rowed crosses. Even this reduced number was not so promising as were those saved from the 6-rowed × 6-rowed crosses, and contained few outstanding types.

HARRY V. HARLAN
MARY L. MARTINI
HARLAND STEVENS

BUREAU OF PLANT INDUSTRY,
U. S. DEPARTMENT OF AGRICULTURE

## THE RECRUDESCENCE OF A CONFUSING TERMINOLOGY

UNTIL the beginning of the present century all popular works on botany, and many of the text-books, failed to distinguish clearly between the sexual and non-sexual phases of plants. Indeed, there appeared from time to time discussions in which either the "homologous" or the "antithetic" nature of the alternation of generations was upheld or disapproved. Yet as early as 1851 Hofmeister had made clear that throughout all the higher groups of the plant kingdom there is a definite alternation of gametophyte and sporophyte—sexual and non-sexual generations. But people continued to speak and write of the pistil as the "female generative organ," and they spoke of the stamens as "male" organs and of "male" cottonwood trees and of "female" pine cones.

Largely through the influence of the text-book by Sydney H. Vines in England and through the teaching of Charles E. Bessey and John M. Coulter in America these ancient inaccuracies of expression disappeared wholly or at least in large degree, so that the former confusion of gametophyte with sporophyte seemed a thing of the past. Practically all writings and text-books distinguished clearly the n- and 2n-generations. This happy state of affairs continued for thirty years, although it must be confessed that our horticultural and agricultural friends remained for most of the time somewhat outside the pale of morphological respectability.

But now, when the former confusion had presumably disappeared from serious botanical literature, up bobs the same old trouble in an otherwise most scholarly and excellent text-book (Wilson and Haber: Introduction to Plant Life, published by Henry Holt and Company, 1937). Students have difficulty enough in distinguishing the sexual from the non-sexual; when the subject is confused in their text-book an impossible situation results. It is much to be hoped that in a second edition the authors of this valuable introduction to botany will adopt a terminology in accord with present cytological knowledge and general conceptions of plant morphology.

FRANCIS RAMALEY

UNIVERSITY OF COLORADO

## HUMAN ARTIFACTS IN ASSOCIATION WITH HORSE AND SLOTH BONES IN SOUTHERN SOUTH AMERICA

WHILE investigating the archeology of the territory along the Straits of Magellan for the American Museum of Natural History, positive evidence of the association of man with extinct horses and sloth was found in two caves. One of these caves is located in the Rio Chico Valley on estancia North Arm, just south of the Argentine-Chilean boundary; the other is about twenty miles east in Dicky Section of estancia Delgado.

In each cave the oldest cultural débris was mixed with fragments of horse and sloth bones identified by Dr. G. Simpson as *Parahipparion saldiasi* and *Mylodon listai*. Many of the bones have been burned and the long bones of the horse broken for the extraction of marrow. In one cave this oldest material had been isolated by slabs of rock and débris fallen from the cave roof. Among the artifacts associated with these bones the most noteworthy, because of subsequent changes, are the stone lance points with long flaring stems and without barbs. However, these points disappear slightly prior to the extinction of the horse and sloth and are followed by a simple bone point.

At the bottom of the layer containing the bone points are the last of the large extinct animals, after which, for a time, the people subsisted largely on birds and foxes. Among the fox bones are some identified as *Pseudalopex avus*, believed to be extinct at the present time.

In the successive layers, the following culture changes occur: above the bone points are artifacts of

a people who used bolas weights and made stemless triangular stone lance points. They, in turn, were followed by people who used the first points which can positively be identified as intended for arrows. These have stems and barbs and are accompanied by broad, stemmed, hafted knives. Then appear small arrow points, identical with those used by the Ona Indians of Tierra del Fuego. Although the two types of arrow points are found together at the surface of the refuse our work at other sites indicates that they are typical of two distinct groups and that the Ona type is not derived from the early one, at least in this region.

Late historic, horse-using, Tehuelche material is almost totally lacking so that the last occupation of these caves was presumably prior to this historic period. Pottery and polished stone work are lacking from all levels.

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# QUOTATIONS

## THE PROPOSED IRRIGATION TUNNEL UNDER THE ROCKY MOUNTAIN NATIONAL PARK

WHEN any group tries to put through legislation in a hurry, by unusual means and without full opportunity for the opponents to bring forward their arguments, the public has a right to be suspicious. It happens that this is just the fashion in which the plan to drive a power and irrigation tunnel under the Continental Divide and through the Rocky Mountain National Park has been handled in Congress both this year and last.

Last year the project was tacked on to the Interior Department Appropriation Bill on the floor of the Senate, was slipped through and was killed only because strenuous opposition in the House developed during conference. This year a separate bill was regularly introduced by Senator Adams, of Colorado, reported favorably by the Committee on Irrigation and Reclamation, but passed without public hearings or debate. The House has now announced a hearing, but there is danger that the bill will again be hooked on to the Interior Department Appropriation Bill, which has already passed the House, and that it will thus be jammed through without the consideration it deserves. The parliamentary procedure so far used certainly does not reflect confidence on the part of the measure's supporters that it will stand close scrutiny.

There are, indeed, arguments in its favor, as may be learned from the report of Senior Engineer Porter J. Preston, who directed the preparation of preliminary plans and estimates with the aid of a $150,000 PWA allotment. There is little doubt that the ranchers in the Big Thompson Valley on the east side of the divide could make profitable use of the water. There is not much doubt that the hydroelectric power which the scheme would produce could be sold. But the probability that some persons would gain is not a conclusive argument. Some persons would gain, perhaps, if Central Park were taken over for low-rent housing, but certainly the general public would lose.

Whatever the arguments for the project, which will cost anywhere from $24,800,000 for irrigation facilities alone to between $43,000,000 and $60,000,000 if there is a full power development, they should be subjected to an exhaustive public inquiry before they are accepted. Unless they are far more convincing than they now seem to be, the project ought to be dropped. It is not certain that it will be worth while to add to irrigation facilities in the Big Thompson area—or for that matter in any area under present conditions of agriculture. And it is certain that we ought not to add to them at the risk of setting a precedent which will lead to the despoliation of our national parks.—*The New York Times.*

# SCIENTIFIC BOOKS

## ADVENTURES IN BIRD PROTECTION

*Adventures in Bird Protection. An autobiography.* By THOMAS GILBERT PEARSON. Pp. xiv + 459. Appleton-Century, N. Y. $3.50.

IMPORTANT as the topic is yet one may rightly say that this book is far more than its title implies. Its opening chapters paint a vivid picture in plain colors of the early life of a Quaker boy reared under simple circumstances in the South and struggling against adverse conditions to win an education and at the same time follow up the study of birds on which his heart was set. Out of this grows the story not merely of bird protection but even more that of wild life conservation, which has assumed such large proportions in the last fifty years.

Many men see opportunities, but few grasp them. Probably others have recognized as clearly the value of college museums, but he sold the idea to the president of a struggling institution and built up the first college museum in North Carolina. Deeply impressed by the unrestrained slaughter of song birds he appealed alone

to the state legislature, drew up a bill to control the destruction, aroused public support and secured the establishment of the first game warden system in any southern state along lines at once so sane and so successful that the plan was followed for many years in other states as well.

Out of such achievements grew naturally the National Association of Audubon Societies in 1905, in which he was first its secretary and then president, but always at the front of the fight for the conservation of wild life. His tact, his resourcefulness and his persuasive power served to carry through successfully measures in many states, north and south, for game protection, despite powerful opposition. Probably the best known as also the greatest of these battles was that in New York state and later in Congress to put an end to the traffic in bird plumage sold for millinery. This carried his work beyond the limits of the United States and resulted in similar movements in many other countries and in the organization of the important International Committee for Bird Preservation in which he still retains an influential position. The origin and growth of these and numerous other valuable scientific movements are sketched by Dr. Pearson in accurate and unassuming fashion.

The quaint style of the author, the vein of quiet humor which runs through the book, the frank attack upon excesses wherever manifested and the tolerant spirit which has characterized his attitude throughout all the controversies in which he has been engaged are responsible in large measure for the remarkable success which has attended his efforts. This feature stands out clearly in his book. It is a veritable mine of information concerning men and movements in conservation. It covers well the history of the movement during the last fifty years, and the material is presented with a frankness and fairness that is unusual and that makes this record of permanent value.

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## DIESEL ENGINEERING

*Elements of Diesel Engineering.* By ORVILLE ADAMS. Pp. xvi + 478. 250 figures, New York, Henley, 1936. $4.00.

THE book presents the elements of the subject in a clear and concise manner—from the earliest design to the most modern development. The operating principles of the various forms of Diesel construction are presented with a minimum of mathematics and irrelevant detail, consistent with a clear presentation of the subject. Topics of such major importance as fuel injection, fuel pump design, injection nozzles, combustion chamber designs, etc., are treated in such a way as to give a new man in the field an understanding of many of the fine points as well as the basic principles and the present status of development.

The many and varied problems that have been encountered in the development of the Diesel are outlined, and their solutions—or the progress that has been made toward these solutions, with particular emphasis upon the development of the high-speed Diesel—are discussed at length. Such topics as selection, installation, inspection, operation and maintenance of the automotive Diesel engine occupy a relatively large space, which is in keeping with the importance of this phase of the subject, particularly to those persons looking to this field as a means of livelihood.

One gets from studying the book a very good picture of the entire field and the great development that has been made in the Diesel engine, without getting the impression that all the problems have been solved. It is a record of the important background and present state of an industry which, although still in its infancy, has already developed to a place of great importance.

The subject-matter is particularly well selected and organized to serve as a text in a classroom or for individual use in obtaining a thorough picture of the elements of Diesel engineering.

THOS. C. POULTER

# SPECIAL ARTICLES

## THE ORIGIN OF THE AFTER-FEATHER[1] IN FOWL: A PROCESS OF TWINNING

IN 1932[2] we emphasized the origin of the barbs of the definitive feather from a single center situated at or near the mid-ventral line of the formative ring of cells ("collar") surrounding the base of the feather germ and enclosing the neck of the pulp. From this results the invariable seriation of barbs both as to time of origin and apico-basal order in the definitive feather. Though Hosker[3] has questioned this conclusion, further study has served only to confirm it. We shall designate the place of origin of barbs as the *ventral locus*; it has a central position in the "ventral triangle" of our former paper. The other postulates of our pre-

[1] We use Studer's term "after-feather" (Afterfeder) for the small fluffy feather emerging from the superior umbilicus of the contour feathers of most carinate birds. The commonly accepted designation of this feather as aftershaft or hyporhachis is confusing, because the after-feather is a complete feather with its own shaft, barbs and barbules, though of course without a separate calamus of its own. (For current terminology of the feather see Asa C. Chandler, *Univ. of Calif. Publ. in Zool.*, 13: 243–446, 1916.)

[2] Frank R. Lillie and Mary Juhn, *Physiol. Zool.*, 5: 124–184, 1932.

[3] Anne Hosker, *Philos. Trans. of the Roy. Soc. of London*, Sec. B, 226: 143–188, 1936.

vious paper, such as a gradient of activity from mid-ventral to mid-dorsal positions in the collar, and the concrescence theory do not enter into the present considerations.

At the ventral locus, prior to origin of the after-feather, barb primordia are constantly being initiated on both sides of the formative center located here. This bilateral activity is a fundamental feature of the formative center. When, in the fowl, regenerating feathers of the breast or saddle have reached a length of about 5.5 cm, which occurs after about 33 to 35 days of regeneration in the breast, and after about 40 days in the saddle, barbs begin to arise in the center of the ventral triangle instead of at the sides. These have a strictly vertical arrangement instead of an inclination parallel to the sides of the ventral triangle characteristic of their predecessors. When about six to eight of these have formed it is seen that there are now two ventral triangles, one at each side of the vertical barbs. It is inferred that division of the formative center at the ventral locus has taken place. It is then observed that, as each of the daughter formative centers has the same bilateral type of activity as the parent one, they are gradually forced farther and farther apart by the two series of barbs formed between them. At the meeting point of the two series of barbs between the daughter centers a new feather shaft (the hyporhachis) arises. The barbs formed on the opposite sides of the respective formative centers belong to the main feather. Seriation of barbs is identical in the after-feather and the corresponding part of the main feather.

As developing feathers have their ventral surfaces apposed to the pulp, these surfaces of the main feather and its appurtenant after-feather are also apposed to one another when regeneration is completed. They are thus mirror images of one another. In most breeds of fowl, and very generally in birds, the fluffy part of the feather, to the lower part of which the after-feather corresponds, is without pigment pattern; but in the barred rock fowl the barring is continued to the base of the feather and corresponds in the main and after-feather. In the hybrids between barred rock and brown leghorn, pigment pattern is usually absent in the fluffy part, but is occasionally represented by incomplete bars, or asymmetrical spots of black, on a white background. When this happens the asymmetries in the main and the after-feather are mirror images, occurring in quite exact correspondence on the right side of the one and the left side of the other. This test of twinning also thus holds for the after-feather.

Miss Hosker[3] deserves credit for the first records of stages of development of the after-feather; but the incompleteness of her material did not enable her to reach correct conclusions. Total preparations are indispensable for the study of this subject; these are prepared by splitting the cylinder of epidermal cells surrounding the pulp, as described in our former paper, spreading it out flat and fixing it under pressure between two glass slides. Our preparations show every stage in the formation of the after-feather from the origin of its first barbs to its completion. Sections made in different planes furnish valuable supplementary evidence.

The division of the formative center and the mirrored correspondence of patterns between the main feather and the after-feather demonstrate that this phenomenon belongs in the category of twinning. As a corollary, the formation of two feathers after division of the formative center demonstrates that the latter has properties with reference to the formation of the feather comparable to those of the primitive streak or blastopore with reference to the formation of the axis of the embryo. These conclusions are limited for the present to the material actually investigated.

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## THE INFLUENCE OF ELECTROLYTES ON THE OXYGEN DISSOCIATION OF HEMOGLOBIN[1]

NUMEROUS have been the attempts to interpret the equilibrium between oxygen and hemoglobin since Hüffner's first contribution 36 years ago. Adair's intermediate compound hypothesis,[2] a theory which led to an equation with four constants, successfully expressed his own data; Ferry and Green,[3] however, were forced to change the values of these four constants, in order to adapt the equation to their results. In view of this lack of agreement, it was clear that the fundamental assumptions had to be reconsidered.

When blood ferri hemin, dissolved in phosphate and borate buffers of identical pH value, was titrated potentiometrically with a reductant, the $E'_0$ values in phosphate buffer were 38 millivolts more positive than those of hemin in borate buffer. Hemin, on combining with phosphate and borate, formed complex compounds possessing different free energies (Fig. 1). Hemoglobin, like hemin, combined with a number of anions (chloride, sulfate, citrate, phosphate, bicarbonate) giving complex compounds possessing different dissociation constants for the reaction Hb + anion $\rightleftarrows$ Hb anion and the reaction Hb anion + $O_2 \rightleftarrows$ Hb anion $O_2$. This is clearly demonstrated in the experiments plotted in Fig. 2, where the per cent. of $HbO_2$

[1] From the Lasker Foundation for Medical Research, Department of Medicine, and the George Herbert Jones Chemical Laboratory, the University of Chicago.

[2] G. S. Adair, *Jour. Biol. Chem.*, 63: 529, 1925.

[3] R. M. Ferry and A. A. Green, *Jour. Biol. Chem.*, 81: 175, 1929.

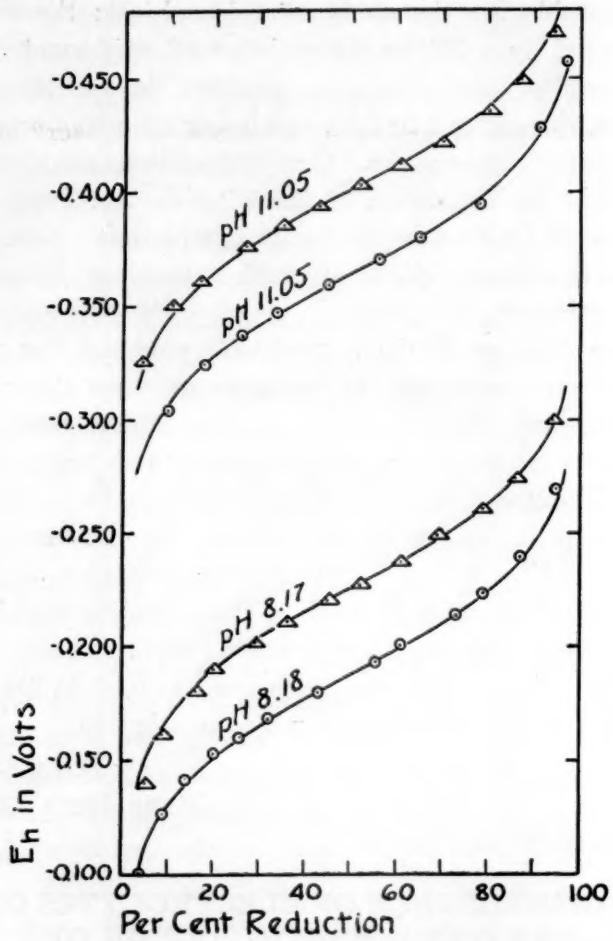


FIG. 1. The effect of anions on the oxidation-reduction potential of blood hemin. Concentration of hemin, 0.0001 M per liter. Titrated with $Na_2S_2O_4$; temp., 30°. ⊙ represents hemin in phosphate buffer; △, hemin in borate buffer.

has been plotted against the concentration of added salts. The experiments were performed with human dialyzed hemoglobin (2 mM $HbO_2$ per liter), at 5 mm $pO_2$, 25°, and pH 6.8. Salt-free hemoglobin possessed the greatest affinity, 50 per cent. $HbO_2$ being reached at 1.05 mm $pO_2$; then came, in decreasing order, Hb chloride, Hb sulfate (not in the figure), Hb citrate (not in the figure), Hb phosphate and Hb bicarbonate. Of course in this last case the picture is complicated by the simultaneous formation of carbamino compounds, the hemoglobin having been kept in mixtures of $NaHCO_3$: $CO_2$. Thus, on increasing the $NaHCO_3$: $CO_2$ concentration and keeping the hydrogen ion concentration *constant,* the affinity of hemoglobin for oxygen is diminished, a phenomenon of great value for facilitating the diffusion of oxygen from the hemoglobin to the tissues. Curiously enough, this oxygen dissociation curve of hemoglobin bicarbonate is almost a replica of the curve drawn from the data of Henderson, Bock, Field and Stoddard,[4] where the authors attributed this diminished affinity to pH changes. In the experiments reported in Fig. 2 we were dealing in every instance with mixtures of Hb and Hb anion, since the amount of anion used was not enough to prevent dissociation of the Hb anion com-

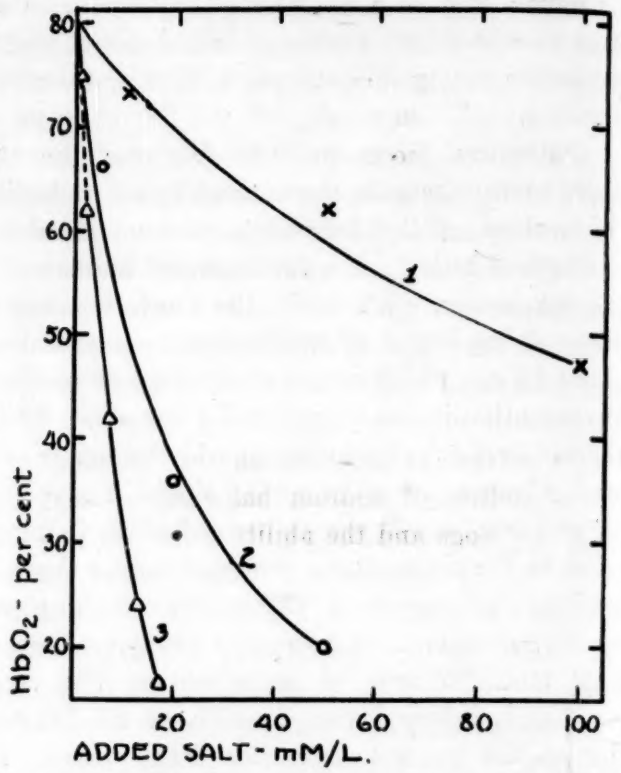


FIG. 2. The effect of anions on the oxygen dissociation of hemoglobin. $HbO_2$ concentration, 2 mM per liter; $pO_2$, 5 mm; pH, 6.8; temp., 25°. *1,* NaCl; *2,* $Na_2HPO_4$: $NaH_2PO_4$ mixture; *3,* $NaHCO_3$: $CO_2$ mixture.

plex. Similar experiments are being performed on the influence of cations.

These experiments show that all previous attempts to interpret the equilibrium between oxygen and hemoglobin have failed, because the influence of electrolytes on the equilibrium by formation of complex compounds was neglected. In all these experiments the equilibrium measured was that of Hb plus unsaturated mixtures of Hb complexes, each of them possessing different dissociation constants.

The $HbO_2$ determinations were made with the photoelectric spectrophotometer described by Hogness, Zscheile and Sidwell.[5]

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## THE "SODIUM RETAINING EFFECT" OF THE SEX HORMONES

THE positive effect of injections of adrenal cortical hormone on the renal excretion of sodium in normal human subjects[1] and in normal dogs[2] has prompted an investigation of the possible effect of sex hormones on the renal excretion of sodium. The similarity in

[4] L. J. Henderson, A. V. Bock, H. Field, Jr. and J. L. Stoddard, *Jour. Biol. Chem.,* 59: 379, 1924.

[5] T. R. Hogness, F. P. Zscheile, Jr., and A. E. Sidwell, *Jour. Phys. Chem.,* 41: 379, 1937.

[1] G. W. Thorn, H. R. Garbutt, F. A. Hitchcock and F. A. Hartman, *Proc. Soc. Exp. Biol. Med.,* 35: 247, 1936.

[2] G. A. Harrop and G. W. Thorn, *Jour. Exp. Med,* 65: 757, 1937.

the chemical structure of corticosterone[3,4] and the sex hormones would indicate the possibility of one or more common physiological properties. The prolonged survival of animals adrenalectomized during pregnancy and heat[5,6] and the favorable influence of the induction of estrus in adrenalectomized dogs[7] make it appear probable that a high concentration of sex hormone is beneficial to adrenalectomized animals.

In the present study the authors have injected crystalline fractions of sex hormones into normal male and female dogs. The dogs were maintained under uniform conditions which included a constant fluid and mineral intake. The effect on the twenty-four-hour renal excretion of sodium has been observed. The care of the dogs and the ability to interpret quantitatively such changes in sodium excretion have been described elsewhere.[8] The "sodium retaining effect" of equivalent amounts of crystalline material has been compared to the effect produced by the injection of a known quantity of standardized adrenal cortical extract. For convenience the result has been expressed as "dog units."

The subcutaneous injection of five milligrams of estradiol resulted in a marked and rather prolonged period of decreased sodium excretion in a normal male dog (Table I). The decreased sodium excretion was

TABLE I

THE EFFECT OF ESTRADIOL ON THE RENAL EXCRETION OF SODIUM IN THE NORMAL DOG

| Day | Urine Vol. cc. | Sodium m. eq. | |
|---|---|---|---|
| 1 | 425 | 55.2 | Control period* |
| 2 | 305 | 32.5 | Subcutaneous injection of 5 mgm. of estradiol at 10 A.M. |
| 3 | 310 | 39.5 | |
| 4 | 305 | 37.1 | |
| 5 | 440 | 60.6 | |
| 6 | 425 | 57.6 | |
| 7 | 515 | 73.0 | |
| 8 | 510 | 73.2 | |
| 9 | 410 | 50.3 | |
| 10 | 410 | 56.1 | |

* Maximum normal daily deviation of twenty-four sodium excretion does not exceed 3 m. eq.

accompanied by a reduced urine output. As the effect of the hormone diminished an increased excretion of sodium was noted ("Rebound"). Continued injections of estrogenic material (Amniotin, 100,000 International Units) into normal male and female dogs did not prevent an ultimate return of sodium excretion to its previous normal level.

[3] I. Reichstein, *Helv. Chim. Acta*, 19: 29, 1936.

[4] E. C. Kendall, H. L. Mason, W. M. Hoehn and B. F. McKenzie, *Prof. Staff Meeting Mayo Clinic*, 12: 136, 1937.

[5] H. A. Stewart, XVII International Congress of Medicine. London, 1913, 173.

[6] J. M. Rogoff and G. N. Stewart, *Am. Jour. Physiol.*, 79: 508, 1927.

[7] W. W. Swingle, W. M. Parkins, A. R. Taylor and J. A. Morrell, *Proc. Soc. Exp. Biol. Med.*, 34: 94, 1936.

[8] G. A. Harrop and G. W. Thorn, *op. cit.*

A comparison has been made of the "sodium retaining effect" of several of the sex hormones (Table II).

TABLE II

A COMPARISON OF THE "SODIUM RETAINING EFFECT" OF SEX HORMONES

| Substance* | Quantity | Assay in dog units |
|---|---|---|
| Estradiol (crystalline) ..... | 0.010 | 700 |
| Progesterone (crystalline) .... | 0.010 | 400 |
| Estrone (crystalline) ..... | 0.010 | 200+ |
| Pregnandiol (crystalline) .... | 0.010 | 140 |
| Testosterone (crystalline) .... | 0.010 | 80 |
| Testosterone proprionic acid ester ..... | 0.010 | 25+ |

* Each substance was taken up in corn oil and injected subcutaneously.

All the sex hormones thus far investigated have displayed some degree of "sodium retaining effect." Estradiol and progesterone appear to be the most active substances in this respect. It is interesting to note that pregnandiol, a substance not known to have physiological activity as a sex hormone, also displayed the "sodium retaining effect." The relationship of the chemical structure of these substances to that of the adrenal cortical hormone is under investigation. It would appear that a possible explanation of the beneficial effect of estrus and pregnancy on the survival of the adrenalectomized bitch might be accounted for on the basis of the salt and water retention induced by the presence of an excess of the sex hormones. It is not known whether this action is a direct one or mediated through some other endocrine gland.

The single injection of 0.017 gms of estradiol in a patient with Addison's disease, maintained on a diet constant in fluid and mineral content, resulted in a retention of sodium, chloride and water, associated with a gain in body weight and an increase in blood pressure. The duration of this effect was seventy-two hours.

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## THE COUMARIN CONTENT OF MELILOTUS DENTATA[1]

IN 1934 one of us (B.) reported the occurrence of a non-bitter form of Melilotus.[2] The non-bitter race did not conform closely in its morphology to any of the described species of sweet clover, so that there was

[1] Papers from the Departments of Genetics (No. 210) and Agricultural Chemistry, Agricultural Experiment Station, University of Wisconsin. Published with the approval of the director of the station. Experiments conducted in cooperation with Division of Forage Crops and Diseases, Bureau of Plant Industry, U. S. Dept. of Agriculture.

[2] SCIENCE, 79: 301.

considerable doubt concerning its classification at that time. The authors are indebted to B. L. Robinson, of the Gray Herbarium, and H. Harms and O. E. Schulz, of the Botanisches Museum, Berlin, for having identified this sweet clover since as an annual flowering form of the typically biennial *Melilotus dentata* (W. K.) Pers. Schulz describes the species as occurring sparingly from central Europe eastward to central Asia, usually on salty soils. It does not appear to have become naturalized in America.

The non-bitter condition of this one stock of *M. dentata* led us to assemble an extensive collection of the species for further study. We are indebted mainly to several European correspondents for seed. Examination of 28 different lots (27 of which were biennials) mostly from central Europe, but a few from Russia and one from Mongolia, has shown that all are free of the characteristic bitter taste of the common sweet clovers, *M. alba* and *M. officinalis*. Apparently *M. dentata* as a species is typically non-bitter. Suvorov's[3] report on the Russian species of sweet clover bears out this conclusion.

As the bitterness of the common sweet clovers is due mainly, if not entirely, to coumarin and closely related substances, it was anticipated that *M. dentata* would differ in its content of these compounds. The analytical findings show clearly that this is the case. Roberts and Link have recently developed a micro-method, to be described elsewhere, for estimating coumarin, melilotic acid and coumaric acid, which not only permits the determination of these substances separately but to an accuracy of about 0.001 per cent. on the dry basis. The earlier methods of Obermayer,[4] Kanewskaja and Fedorowa,[5] Duncan and Dustman[6] and Clayton and Larmour[7] severally encounter various analytical difficulties, such as failure to separate the three constituents, inclusion of other phenolic substances in the coumarin fraction and interference by plant pigments. These disadvantages are largely overcome by the procedure used in the present investigation.

Using the highly refined method of Roberts and Link no coumarin, melilotic acid or coumaric acid were detected in the vegetative tissues of *M. dentata* at the flowering stage. Seven different races were tested as follows: F.P.I. 90753, Botanic Garden, Peiping, China; Botanic Garden, Copenhagen, Denmark; Thüringen and Saxony, Germany; Moravia, Czechoslovakia; Saratov and West Siberia, U.S.S.R.; Altai Mountains, Mongolia. All these stocks, except those from the botanical gardens and possibly that from Saratov, represent the forms indigenous to these respective regions, according to the information supplied by the correspondents to whom we are indebted for the seed. It is probable, therefore, that if these substances are present at all in the leaves and stems of *M. dentata*, the amounts are less than 0.001 per cent.

A sample of common yellow sweet clover, *M. officinalis*, analyzed at the same stage of development, was found to contain 0.65 per cent. coumarin, 0.25 per cent. melilotic acid and 0.036 per cent. coumaric acid. The corresponding values for a commercial strain of common white sweet clover, *M. alba*, were found to be 0.36 per cent., 0.27 per cent. and 0.048 per cent. The common sweet clovers vary rather widely in composition from strain to strain and at different stages of development so that the above results are not necessarily representative of the respective species.

A small amount of coumarin is present in the seed of *M. dentata*. Analysis of three of the above-mentioned stocks (Peiping, Copenhagen and Moravia) showed 0.021 per cent., 0.074 per cent. and 0.040 per cent., respectively, on the dry basis. A sample of *M. officinalis* seed run concurrently was found to contain 0.63 per cent. coumarin and an *M. alba* lot, 0.46 per cent. It will be noted that these values are roughly ten times as high as those for *M. dentata*. That the material determined as coumarin in the analysis of the seed is actually that substance was shown by the isolation of 25 mg of pure coumarin from 31 g of *M. dentata* (Copenhagen strain) seed. The melting point of the isolated material and the mixed melting point with pure coumarin were 71.0–71.5° C., the same as that for pure coumarin. The iodine-potassium iodide test and certain coupling tests were positive, and the chemical characteristics exhibited during the isolation were identical with those of coumarin. The regular method of analysis indicates that if any melilotic acid and coumaric acid occur in the seed of *M. dentata* the amounts are extremely small.

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[3] Semenovodstvo, No. 2 (quoted from Herb. Abstr. 5: 153).
[4] *Zeits. Anal. Chem.*, 52: 172–191.
[5] *Ibid.*, 93: 176–180.
[6] *Jour. Ind. Eng. Chem.*, 6: 210–213.
[7] *Can. Jour. Res.* (C) 13: 89–100.

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